

III. "On the Action of Nitric Acid and of Binoxide of Manganese and Sulphuric Acid on the Organic Bases." By A. MATTHIESSEN, Ph.D. Communicated by Prof. STOKES, Sec. R.S. Received February 3, 1859.

In the Proceedings of the Royal Society (vol. ix. p. 118), I stated that by the action of nitrous acid on aniline I had obtained ammonia and nitrophenasic acid; since then I have acted on several other of the organic bases with the same reagent, as well as with nitric acid, and with binoxide of manganese and sulphuric acid; and I will now shortly enumerate the experiments.

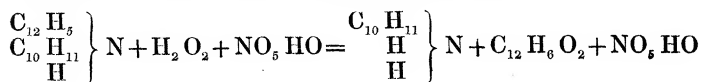
1. *Action of Nitrous Acid on Amylaniline.*

The dilute solution of the nitrate of amylaniline was acted on by nitrous acid at 100° C. for 12 hours. Amylaniline and ammonia were obtained, but in quantities too small to be quantitatively determined.

2. *Action of Nitric Acid on Amylaniline.*

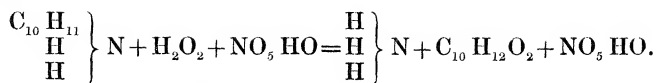
Amylaniline was boiled with dilute nitric acid (1 part acid to 2 of water) until the reaction began, which was immediately stopped by adding cold water to the solution. This was filtered when cold from the nitrophenasic acid, and after potash had been added, it was again filtered to separate any undecomposed amylaniline. The filtrate was distilled, the distillate redistilled *per ascensum* into hydrochloric acid, and the acid solution evaporated to dryness. The residue was then extracted with absolute alcohol, and the filtrate evaporated to dryness. This operation was repeated four or five times. A platinum-salt* made with the chloride, which was soluble in absolute alcohol, gave 33·55 per cent. platinum. The chloroplatinate of amylamine requires 33·66 per cent. The platinum-salt of that chloride which was insoluble in absolute alcohol gave 43·9 per cent. platinum. The chloroplatinate of ammonia requires 44·2 per cent.

The above reaction may be explained as follows:—



* All the platinum-salts determined were recrystallized in water.

and



The free nitric acid present converts the phenylic alcohol into nitrophenasic acid, and the amylic alcohol into nitrite of amyl.

3. Action of Nitric Acid on Ethylaniline.

Ethylaniline was treated in the same manner as amylaniline. The platinum-salt of the chloride which was soluble in absolute alcohol gave in two experiments 39·6 and 39·5 per cent. platinum. The percentage of platinum in chloroplatinate of ethylamine is 39·3.

The platinum-salt of the chloride which was insoluble in absolute alcohol gave 44 per cent. platinum, which agrees with the number required for the chloroplatinate of ammonia.

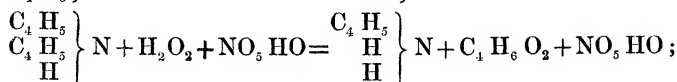
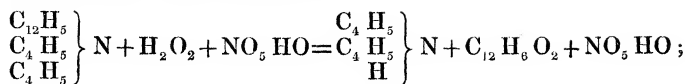
4. Action of Nitric Acid on Diethylaniline.

Diethylaniline was treated with dilute nitric acid (1 part of acid to 4 of water), and heated till the temperature reached 54° C., when, on being left to itself, it soon became turbid, and the temperature rose about 10° C. After a while the solution cleared itself again, but remained very dark. When quite cold, it was filtered from the nitrophenasic acid, and the filtrate was treated in the same manner as described in Experiment 2. The solution of the chlorides (5–6 grms. were obtained from about 50 of diethylaniline), which were soluble in absolute alcohol, was partially precipitated with bichloride of platinum (precipitate No. 1); then another portion was precipitated, which was not used; after this, more bichloride was added (precipitate No. 2); and lastly, an excess of bichloride was added (precipitate No. 3). The platinum found in the three precipitates was

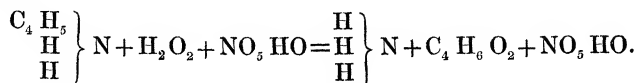
No. 1.	No. 2.	No. 3.
39·2 per cent.	35·5 per cent.	35·4 per cent.

The chloroplatinate of ethylamine contains 39·3 per cent., and of diethylamine 35·3 per cent. platinum. A platinum-salt made with chloride insoluble in absolute alcohol, gave 44·2 per cent. platinum, which is exactly the amount contained in the chloroplatinate of ammonia.

The reaction was as follows :—



and



As in the case of amylaniline, the phenylic alcohol and the alcohol are converted into nitrophenasic acid and nitrite of ethyl; the ammonia being in both cases partially oxidized.

5. *Action of Binoxide of Manganese and Sulphuric Acid on Aniline.*

Aniline was dissolved in an excess of dilute sulphuric acid (1 part of acid to 6 of water) and heated to boiling, when a small quantity of binoxide of manganese was added. The reaction was allowed to continue for 3 or 4 minutes, and it was stopped by cooling the flask in water. Potash was then added, and the solution filtered. The filtrate was distilled as described in experiment 2, and the distillate evaporated to dryness with hydrochloric acid, and extracted with absolute alcohol, to dissolve any chloride of aniline present. A platinum-salt made from the chloride, insoluble in absolute alcohol, gave 44.0 per cent. platinum, which corresponds to the platinum in the chloroplatinate of ammonia.

6. *Action of Binoxide of Manganese and Sulphuric Acid on Diethylaniline.*

Diethylaniline was treated in the same manner as aniline, but only for about one minute. Potash was added, &c., as in the foregoing experiment. The platinum-salt partially precipitated, as in Experiment 4, from the chloride soluble in absolute alcohol, gave :—

Precipitate No. 1.
37.6 per cent.

Precipitate No. 2.
35.4 per cent. platinum.

No. 1 appears to be only a mixture of the chloroplatinates of ethylamine and diethylamine; the quantity of salt first precipitated being too small to be properly recrystallized (on account of former experiments showing that the quantity of ethylamine present was very small). No. 2 corresponds with diethylamine, and of this salt

there was a large quantity, so that it was recrystallized twice. A platinum-salt made from the chloride insoluble in absolute alcohol (of which there was only a very small quantity), gave 44·3 per cent. platinum, which is almost the same as the amount in chloroplatinate of ammonia. No phenylic alcohol was found nor any of its compounds; and according to an experiment of Long (not yet published), on the oxidation of phenylic alcohol, that chemist always, excepting when he used spongy platinum, obtained a resinous mass.

From the above experiments, it appears that by the action of nitrous acid, nitric acid, binoxide of manganese and sulphuric acid, permanganate of potash*, potash†, and in some cases by the presence of acids alone (as sulphuric or hydrochloric)‡, on the organic bases in the presence of water, water only is decomposed in the first stage of the reaction; and the fact that the radicals contained in the bases are replaced by hydrogen by degrees, makes it plausible that by these means we may be able to determine the constitution of the natural organic bases.

I am now experimenting with narcotine, and to all appearance, I shall succeed in determining its constitution.

In conclusion, I may here be allowed to thank Dr. Holzmann for his assistance in carrying out the above experiments.

February 10, 1859.

Sir BENJAMIN C. BRODIE, Bart., President, in the Chair.

The following communication was read :—

“Experiments on the Action of Food upon the Respiration.”

By EDWARD SMITH, M.D., LL.B., L.R.C.P., Assistant-Physician to the Hospital for Consumption, Brompton.
Communicated by Sir BENJAMIN C. BRODIE, Bart. Received January 6, 1859.

(Abstract.)

The author had proved in his former Paper that the maximum influence of food is observed within two and a half hours after its

* By its action on aniline, ammonia is obtained. † In its action on the amides.

‡ In the case of asparagine, benzamide, &c.